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(54) Title: PROCESS AND COMPOSITION FOR RAPID MASS PRODUCTION OF HOLOGRAPHIC RECORDING ARTICLE

(57) Abstract: A rapid mass production of the high performance holographic recording articles including the process and composition are described. To prepare a high performance holographic recording article based on two-component urethane matrix system, for example, polyols and all the additives must be virtually free of moisture contents. Deaeration must be carried out, once isocyanate and polyols including catalysts and all other ingredients are mixed together, to eliminate all entrapped air that is introduced into the mixture during mixing. The deaeration takes time, and the urethane reaction must not be allowed to take place until all air bubbles are evacuated from the isocyanate-polyols mixture. The rapid mass production of this invention overcomes such process limitations and results in a high-volume production of the high performance holographic recording articles.

PROCESS AND COMPOSITION FOR RAPID MASS PRODUCTION OF
HOLOGRAPHIC RECORDING ARTICLE

Related Application

5 [0001] This application claims priority from U.S. Provisional Application 60/310,225, filed August 7, 2001, which is entitled the same as this application.

Field of the Invention

[0002] The invention relates to optical articles including holographic recording media, in particular media useful either with holographic storage systems or as 10 components such as optical filters or beam steerers. In particular, this invention relates to rapid mass production of high performance holographic recording article.

Background

[0003] Developers of information storage devices and methods continue to seek increased storage capacity. As part of this development, so-called page-wise memory 15 systems, in particular holographic systems, have been suggested as alternatives to conventional memory devices.

[0004] A hologram stores data in three dimensions and reads an entire page of data at one time, i.e., page-wise, which is unlike an optical CD disk that stores data in two dimensions and reads a track at a time. Page-wise systems involve the storage and 20 readout of an entire two-dimensional representation, e.g., a page, of data. Typically, recording light passes through a two-dimensional array of dark and transparent areas representing data, and the holographic system stores, in three dimensions, holographic representations of the pages as patterns of varying refractive index imprinted into a storage medium. Holographic systems are discussed generally in D. Psaltis et al., 25 "Holographic Memories," Scientific American, November 1995, the disclosure of which is hereby incorporated by reference. One method of holographic storage is phase correlation multiplex holography, which is described in U.S. Patent No. 5,719,691 issued February 17, 1998, the disclosure of which is hereby incorporated by reference.

[0005] The advantages of recording a hologram are high density (storage of hundreds 30 of billions of bytes of data), high speed (transfer rate of a billion or more bits per second) and ability to select a randomly chosen data element in 100 microseconds or less. These advantages arise from three-dimensional recording and from simultaneous readout of an entire page of data at one time.

[0006] A hologram is a pattern, also known as a grating, which is formed when two laser beams interfere with each other in a light-sensitive material (LSM) whose optical properties are altered by the intersecting beams. Before the bits of data can be imprinted in this manner in the LSM, they must be represented as a pattern of clear and opaque squares on a display such as a liquid crystal display (LCD) screen, a miniature version of the ones in laptop computers. Other devices such as reflective LCD's or reflective deformable micromirror devices can also be used to represent the data. A blue-green laser beam, for example, is shined through this crossword-puzzelike pattern called a page, and focused by lenses to create a beam known as a signal beam. A hologram of the page of data is created when the signal beam meets another beam, called the reference beam, in the LSM. The reference beam could be collimated, which means that all its light waves are synchronized, with crests and troughs passing through a plane in lockstep. Such waves are known as plane waves. The reference beam may also be a spherical beam or may be phase-encoded or structured in other manners well known in the field of holography. The grating created when the signal and reference beams meet is captured as a pattern of varying refractivity in the LSM.

[0007] After recording the grating, the page can be holographically reconstructed by for example shining the reference beam into the LSM from the same angle at which it had entered the LSM to create the hologram. As it passes through the grating in the LSM, the reference beam is diffracted in such a way that it recreates the image of the original page and the information contained on it. A reconstructed page is then projected onto a detector such as an array of electrooptical detectors that sense the light-and-dark pattern, thereby reading all the stored information on the page at once. The data can then be electronically stored, accessed or manipulated by any conventional computer.

[0008] In one embodiment of phase correlation multiplex holography, a reference light beam is passed through a phase mask, and intersected in the recording medium with a signal beam that has passed through an array representing data, thereby forming a hologram in the medium. The spatial relation of the phase mask and the reference beam is adjusted for each successive page of data, thereby modulating the phase of the reference beam and allowing the data to be stored at overlapping areas in the medium. The data is later reconstructed by passing a reference beam through the original storage location with the same phase modulation used during data storage. It is also possible to use volume holograms as passive optical components to control or modify light directed

at the medium, e.g., filters or beam steerers. Writing processes that provide refractive index changes are also capable of forming articles such as waveguides.

[0009] The capabilities of holographic storage systems are limited in part by the storage media. Iron-doped lithium niobate has been used as a storage medium for

5 research purposes for many years. However, lithium niobate is expensive, exhibits poor sensitivity (1 J/cm^2), has low index contrast (Δn of about 10^{-4}), and exhibits destructive read-out (i.e., images are destroyed upon reading). Alternatives have therefore been sought, particularly in the area of photosensitive polymer films. See, e.g., W.K.

10 Smothers et al., "Photopolymers for Holography," SPIE OE/Laser Conference, 1212-03, Los Angeles, CA, 1990. The material described in this article contains a photoimageable

system containing a liquid monomer material (the photoactive monomer) and a photoinitiator (which promotes the polymerization of the monomer upon exposure to light), where the photoimageable system is in an organic polymer host matrix that is substantially inert to the exposure light. During writing of information into the material

15 (by passing recording light through an array representing data), the monomer polymerizes in the exposed regions. Due to the lowering of the monomer concentration caused by the polymerization, monomer from the dark, unexposed regions of the material diffuses to the exposed regions. The polymerization and resulting concentration gradient create a refractive index change, forming the hologram representing the data. Unfortunately,

20 deposition onto a substrate of the pre-formed matrix material containing the photoimageable system requires use of solvent, and the thickness of the material is therefore limited, e.g., to no more than about $150 \mu\text{m}$, to allow enough evaporation of the solvent to attain a stable material and reduce void formation. In holographic processes

such as described above, which utilize three-dimensional space of a medium, the storage 25 capacity is proportional to a medium's thickness. Thus, the need for solvent removal inhibits the storage capacity of a medium. (Holography of this type is typically referred to as volume holography because a Klein-Cook Q parameter greater than 1 is exhibited (see W. Klein and B. Cook, "Unified approach to ultrasonic light diffraction," IEEE Transaction on Sonics and Ultrasonics, SU-14, 1967, at 123-134). In volume holography,

30 the media thickness is generally greater than the fringe spacing.)

[0010] U.S. Patent No. 6,013,454 and application Serial No. 08/698,142, the disclosures of which are hereby incorporated by reference, also relate to a photoimageable system in an organic polymer matrix. In particular, the application

discloses a recording medium formed by polymerizing matrix material *in situ* from a fluid mixture of organic oligomer matrix precursor and a photoimageable system. A similar type of system, but which does not incorporate oligomers, is discussed in D.J. Lougnot et al., *Pure and Appl. Optics*, 2, 383 (1993). Because little or no solvent is typically required for deposition of these matrix materials, greater thicknesses are possible, e.g., 200 μm and above. However, while useful results are obtained by such processes, the possibility exists for reaction between the precursors to the matrix polymer and the photoactive monomer. Such reaction would reduce the refractive index contrast between the matrix and the polymerized photoactive monomer, thereby affecting to an extent the strength of the stored hologram.

[0011] Thus, while progress has been made in fabricating photorecording media suitable for use in holographic storage systems, further progress is desirable. In particular, rapid production of high performance holographic media which are capable of being formed in relatively thick layers, e.g., greater than 200 μm , which substantially avoid reaction between the matrix material and photomonomer, and which exhibit useful holographic properties, are desired.

SUMMARY OF THE INVENTION

[0012] This invention in high performance holographic recording articles is based on a thermally crosslinked matrix system containing photoimageable monomers. Fabrication of such system demanded that the article is of low scatter, bubble-free, optically flat, and uniform in thickness so that the articles will be of high optical quality and that the articles formed will have the desired dynamic range and photosensitivity.

[0013] To meet such optical quality requirements, care must be taken to deaerate all components before their reaction is activated either by heat or catalysts. Additionally, any impurity that can produce gases as byproducts must be eliminated to prevent bubbles formation in the cured final matrix system.

[0014] In addition, it is desirable that the formation of the thermally crosslinked matrix system occurs rapidly (preferably less than 20 minutes) to enable mass production of the recording media.

[0015] To prepare a high performance holographic recording article based on two-component urethane matrix system, for example, polyols and all the additives must be virtually free of moisture contents. Deaeration must be carried out, once isocyanate and

polyols including catalysts and all other ingredients are mixed together, to eliminate all entrapped air that is introduced into the mixture during mixing. The deaeration takes time, and the urethane reaction must not be allowed to take place until all air bubbles are evacuated from the isocyanate- polyols mixture. As such, the process limits high-volume
5 production of the high performance holographic recording articles.

[0016] Polyols are selected from diols and triols of polytetramethylene glycol, polycaprolactone, polypropylene oxide. Preferred polyols are polypropylene oxide triols with molecular weight ranging from 450 to 6,000. Preferably the polyols are free of moisture contents. High temperature vacuum distillation treatments or additives such as
10 moisture scavengers may be used to assure no water residue remains in the polyols before use.

[0017] Additives include thermal stabilizers such as butyrated hydroxytoluene (BHT), Phenothiazine, hydroquinone, and methylether of hydroquinone; reducers such as peroxides, phosphites, and hydroxyamines; and deformers or deaerators to eliminate
15 entrapped air bubbles.

[0018] Tin catalysts could be used. These are dimethyltindilaurate, dibutyltindilaurate, stannous octoate, and others.

[0019] The invention constitutes an improvement over prior recording media. Prior art has described thermally cross-linked matrix/photoimageable monomer systems but
20 have not described methods that enable their rapid fabrication.

[0020] The invention's use of a matrix precursor (i.e., the one or more compounds from which the matrix is formed) and a photoactive monomer the polymerize by independent reactions substantially prevents both cross-reaction between the photoactive monomer and the matrix precursor during the cure, and inhibition of subsequent
25 monomer polymerization. Use of a matrix precursor and photoactive monomer that form compatible polymers substantially avoids phase separation. And *in situ* formation allows fabrication of media with desirable thicknesses. The matrix precursors are chosen to facilitate rapid production of the recording media (i.e., precursors that polymerize rapidly). In addition, the recording media is fabricated through the use of an automated
30 mixing system to further facilitate efficient production of the recording media.

[0021] In addition to recording media, these material properties are also useful for forming a variety of optical articles (optical articles being articles that rely on the formation of refractive index patterns or modulations in the refractive index to control or modify light that is directed at them). Such articles include, but are not limited to, optical

waveguides, beam steerers, and optical filters. Independent reactions indicate: (a) the reactions proceed by different types of reaction intermediates, e.g., ionic vs. free radical, (b) neither the intermediate nor the conditions by which the matrix is polymerized will induce substantial polymerization of the photoactive monomer functional groups, i.e., the group or groups on a photoactive monomer that are the reaction sites for polymerization during the pattern (e.g., hologram) writing process (substantial polymerization indicates polymerization of more than 20% of the monomer functional groups), and (c) neither the intermediate nor the conditions by which the matrix is polymerized will induce a non-polymerization reaction of the monomer functional groups that either causes cross-reaction between monomer functional groups and the matrix or inhibits later polymerization of the monomer functional groups.

10 [0022] Polymers are considered to be compatible if a blend of the polymers is characterized, in 90° light scattering of a wavelength used for hologram formation, by a Rayleigh ratio (R_{90°) less than $7 \times 10^{-3} \text{ cm}^{-1}$. The Rayleigh ratio (R_θ) is a conventionally known property, and is defined as the energy scattered by a unit volume in the direction θ , per steradian, when a medium is illuminated with a unit intensity of unpolarized light, as discussed in M. Kerker, The Scattering of Light and Other Electromagnetic Radiation, Academic Press, San Diego, 1969, at 38. The Rayleigh ratio is typically obtained by comparison to the energy scatter of a reference material having a known Rayleigh ratio.

15 20 Polymers which are considered to be miscible, e.g., according to conventional tests such as exhibition of a single glass transition temperature, will typically be compatible as well. But polymers that are compatible will not necessarily be miscible. *In situ* indicates that the matrix is cured in the presence of the photoimageable system. A useful photorecording material, i.e., the matrix material plus the photoactive monomer, 25 photoinitiator, and/or other additives, is attained, the material capable of being formed in thicknesses greater than 200 μm , advantageously greater than 500 μm , and, upon flood exposure, exhibiting light scattering properties such that the Rayleigh ratio, R_{90° , is less than 7×10^{-3} . (Flood exposure is exposure of the entire photorecording material by incoherent light at wavelengths suitable to induce substantially complete polymerization 30 of the photoactive monomer throughout the material.)

30 [0023] The optical article of the invention is formed by steps including mixing a matrix precursor and a photoactive monomer, and curing the mixture to form the matrix *in situ*. As discussed previously, the reaction by which the matrix precursor is

polymerized during the cure is independent from the reaction by which the photoactive monomer is later polymerized during writing of a pattern, e.g., data or waveguide form, and, in addition, the matrix polymer and the polymer resulting from polymerization of the photoactive monomer (hereafter referred to as the photopolymer) are compatible with

5 each other. (The matrix is considered to be formed when the photorecording material exhibits an elastic modulus of at least about 10^5 Pa. Curing indicates reacting the matrix precursor such that the matrix provides this elastic modulus in the photorecording material.) The optical article of the invention contains a three-dimensional crosslinked polymer matrix and one or more photoactive monomers. At least one photoactive

10 monomer contains one or more moieties, excluding the monomer functional groups, that are substantially absent from the polymer matrix. (Substantially absent indicates that it is possible to find a moiety in the photoactive monomer such that no more than 20% of all such moieties in the photorecording material are present, i.e., covalently bonded, in the matrix.) The resulting independence between the host matrix and the monomer offers

15 useful recording properties in holographic media and desirable properties in waveguides such as enabling formation of large modulations in the refractive index without the need for high concentrations of the photoactive monomer. Moreover, it is possible to form the material of the invention without the disadvantageous solvent development required previously.

20 [0024] In contrast to a holographic recording medium of the invention, media which utilize a matrix precursor and photoactive monomer that polymerize by non-independent reactions often experience substantial cross-reaction between the precursor and the photoactive monomer during the matrix cure (e.g., greater than 20% of the monomer is reacted or attached to the matrix after cure), or other reactions that inhibit polymerization

25 of the photoactive monomer. Cross-reaction tends to undesirably reduce the refractive index contrast between the matrix and the photoactive monomer and is capable of affecting the subsequent polymerization of the photoactive monomer, and inhibition of monomer polymerization clearly affects the process of writing holograms. As for compatibility, previous work has been concerned with the compatibility of the

30 photoactive monomer in a matrix polymer, not the compatibility of the resulting photopolymer in the matrix. Yet, where the photopolymer and matrix polymer are not compatible, phase separation typically occurs during hologram formation. It is possible for such phase separation to lead to increased light scattering, reflected in haziness or

opacity, thereby degrading the quality of the medium, and the fidelity with which stored data is capable of being recovered.

[0025] A rapid mass production methodology has been invented to fabricate these high performance holographic recording articles incorporating compatibility, miscibility and other aforementioned advantages of the polymer matrix and photoactive monomers. 5 The process and composition are described below.

[0026] Additional advantages of this invention would become readily apparent to those skilled in this art from the following detailed description, wherein only the preferred embodiments of this invention are shown and described, simply by way of illustration of 10 the best mode contemplated for carrying out this invention. As would be realized, this invention is capable of other and different embodiments, and its details are capable of modifications in various obvious respects, all without departing from this invention. Accordingly, the drawings and description are to be regarded as illustrative in nature and not as restrictive.

15 **DETAILED DESCRIPTION OF THE INVENTION**

[0027] The optical article, e.g., holographic recording medium, of the invention is formed by steps including mixing a matrix precursor and a photoactive monomer, and curing the mixture to form the matrix *in situ*. The matrix precursor and photoactive monomer are selected such that (a) the reaction by which the matrix precursor is 20 polymerized during the cure is independent from the reaction by which the photoactive monomer will be polymerized during writing of a pattern, e.g., data, and (b) the matrix polymer and the polymer resulting from polymerization of the photoactive monomer (the photopolymer) are compatible with each other. As discussed previously, the matrix is considered to be formed when the photorecording material, i.e., the matrix material plus 25 the photoactive monomer, photoinitiator, and/or other additives, exhibits an elastic modulus of at least about 10⁵ Pa, generally about 10⁵ Pa to about 10⁹ Pa, advantageously about 10⁶ Pa to about 10⁸ Pa.

[0028] The compatibility of the matrix polymer and photopolymer tends to prevent 30 large-scale (>100 nm) phase separation of the components, such large-scale phase separation typically leading to undesirable haziness or opacity. Utilization of a photoactive monomer and a matrix precursor that polymerize by independent reactions provides a cured matrix substantially free of cross-reaction, i.e., the photoactive monomer remains substantially inert during the matrix cure. In addition, due to the independent reactions, there is no inhibition of subsequent polymerization of the photoactive

monomer. At least one photoactive monomer contains one or more moieties, excluding the monomer functional groups, that are substantially absent from the polymer matrix, i.e., it is possible to find a moiety in the photoactive monomer such that no more than 20% of all such moieties in the photorecording material are present, i.e., covalently bonded, in the matrix. The resulting optical article is capable of exhibiting desirable refractive index contrast due to the independence of the matrix from the photoactive monomer.

5 [0029] As discussed above, formation of a hologram, waveguide, or other optical article relies on a refractive index contrast (Δn) between exposed and unexposed regions of a medium, this contrast at least partly due to monomer diffusion to exposed regions. High index contrast is desired because it provides improved signal strength when reading a hologram, and provides efficient confinement of an optical wave in a waveguide. One way to provide high index contrast in the invention is to use a photoactive monomer having moieties (referred to as index-contrasting moieties) that are substantially absent

10 from the matrix, and that exhibit a refractive index substantially different from the index exhibited by the bulk of the matrix. For example, high contrast would be obtained by using a matrix that contains primarily aliphatic or saturated alicyclic moieties with a low concentration of heavy atoms and conjugated double bonds (providing low index) and a photoactive monomer made up primarily of aromatic or similar high-index moieties.

15 [0030] The matrix is a solid polymer formed *in situ* from a matrix precursor by a curing step (curing indicating a step of inducing reaction of the precursor to form the polymeric matrix). It is possible for the precursor to be one or more monomers, one or more oligomers, or a mixture of monomer and oligomer. In addition, it is possible for there to be greater than one type of precursor functional group, either on a single

20 precursor molecule or in a group of precursor molecules. (Precursor functional groups are the group or groups on a precursor molecule that are the reaction sites for polymerization during matrix cure.) To promote mixing with the photoactive monomer, the precursor is advantageously liquid at some temperature between about -50°C and about 80°C. Advantageously, the matrix polymerization is capable of being performed at

25 room temperature. Also advantageously, the polymerization is capable of being performed in a time period less than 5 minutes. The glass transition temperature (T_g) of the photorecording material is advantageously low enough to permit sufficient diffusion and chemical reaction of the photoactive monomer during a holographic recording

process. Generally, the T_g is not more than 50°C above the temperature at which holographic recording is performed, which, for typical holographic recording, means a T_g between about 80°C and about -130°C (as measured by conventional methods).

[0031] Examples of polymerization reactions contemplated for forming matrix

5 polymers in the invention include cationic epoxy polymerization, cationic vinyl ether polymerization, cationic alkenyl ether polymerization, cationic alkyl ether polymerization, cationic ketene acetal polymerization, epoxy-amine step polymerization, epoxy-mercaptopan step polymerization, unsaturated ester-amine step polymerization (via Michael addition), unsaturated ester-mercaptopan step polymerization (via Michael 10 addition), vinyl-silicon hydride step polymerization (hydrosilylation), isocyanate-hydroxyl step polymerization (urethane formation), and isocyanatae-amine step polymerization (urea formation).

[0032] Several such reactions are enabled or accelerated by suitable catalysts. For example, cationic epoxy polymerization takes place rapidly at room temperature by use of 15 BF_3 -based catalysts, other cationic polymerizations proceed in the presence of protons, epoxy-mercaptopan reactions and Michael additions are accelerated by bases such as amines, hydrosilylation proceeds rapidly in the presence of transition metal catalysts such as platinum, and urethane and urea formation proceed rapidly when tin catalysts are employed. It is also possible to use photogenerated catalysts for matrix formation, 20 provided that steps are taken to prevent polymerization of the photoactive monomer during the photogeneration.

[0033] Formulation of a version of high performance holographic recording systems comprises the following ingredients:

NCO-terminated prepolymers	20 - 50 Wt %
Acrylate Monomers	1-15 Wt %
Photoinitiators	0.2 - 3 Wt %
Polyols	40 - 75 Wt %
Catalysts	0.1 - 3 Wt %
Additives	0.001 - 0.5 Wt %

25 [0034] The NCO-terminated prepolymers are selected from the by-products of diols and diisocyanates that have wt % contents of NCO in the range of 10 to 25. The NCO contents were determined based on the prepolymer, unreacted diisocyanate and optionally added neat polyisocyanates to achieve the high performance characteristics. Aromatic

diisocyanates based prepolymers are preferred. However, when the NCO-terminated prepolymer is based on aliphatic diisocyanates, 5 to 100 % of its wt % contents of NCO have to be derived from aromatic diisocyanates or aliphatic polyisocyanates. Preferred aromatic diisocyanates are, but no limit to, diphenylmethane diisocyanate (MDI) and 5 toluene diisocyanate (TDI). Preferred aliphatic polyisocyanates are: Hexamethylene diisocyanate (HDI) and its biuret, isocyanurate, uretidione, and other derivatives.

[0035] The photoactive monomer is any monomer or monomers capable of undergoing photoinitiated polymerization, and which, in combination with a matrix materials, meets the polymerization reaction and compatibility requirements of the 10 invention. Suitable photoactive monomers include those which polymerize by a free-radical reaction, e.g., molecules containing ethylenic unsaturation such as acrylates, methacrylates, acrylamides, methacrylamides, styrene, substituted styrenes, vinyl naphthalene, substituted vinyl naphthalenes, and other vinyl derivatives. Free-radical copolymerizable pair systems such as vinyl ether mixed with maleate and thiol mixed 15 with olefin are also suitable. It is also possible to use cationically polymerizable systems such as vinyl ethers, alkenyl ethers, alkyl ethers, ketene acetals, and epoxies. It is also possible for a single photoactive monomer molecule to contain more than one monomer functional group. As mentioned previously, relatively high index contrast is desired in the article of the invention, whether for improved readout in a recording media or 20 efficient light confinement in a waveguide. In addition, it is advantageous to induce this relatively large index change with a small number of monomer functional groups, because polymerization of the monomer generally induces shrinkage in a material.

[0036] Such shrinkage has a detrimental effect on the retrieval of data from stored 25 holograms, and also degrades the performance of waveguide devices such as by increased transmission losses or other performance deviations. Lowering the number of monomer functional groups that must be polymerized to attain the necessary index contrast is therefore desirable. This lowering is possible by increasing the ratio of the molecular volume of the monomers to the number of monomer functional groups on the monomers. This increase is attainable by incorporating into a monomer larger index-contrasting 30 moieties and/or a larger number of index-contrasting moieties. For example, if the matrix is composed primarily of aliphatic or other low index moieties and the monomer is a higher index species where the higher index is imparted by a benzene ring, the molecular volume could be increased relative to the number of monomer functional groups by incorporating a naphthalene ring instead of a benzene ring (the naphthalene having a

larger volume), or by incorporating one or more additional benzene rings, without increasing the number of monomer functional groups. In this manner, polymerization of a given volume fraction of the monomers with the larger molecular volume/monomer functional group ratio would require polymerization of less monomer functional groups,

5 thereby inducing less shrinkage. But the requisite volume fraction of monomer would still diffuse from the unexposed region to the exposed region, providing the desired refractive index.

[0037] The molecular volume of the monomer, however, should not be so large as to slow diffusion below an acceptable rate. Diffusion rates are controlled by factors

10 including size of diffusing species, viscosity of the medium, and intermolecular interactions. Larger species tend to diffuse more slowly, but it would be possible in some situations to lower the viscosity or make adjustments to the other molecules present in order to raise diffusion to an acceptable level. Also, in accord with the discussion herein, it is important to ensure that larger molecules maintain compatibility with the matrix.

15 [0038] Numerous architectures are possible for monomers containing multiple index-contrasting moieties. For example, it is possible for the moieties to be in the main chain of a linear oligomer, or to be substituents along an oligomer chain. Alternatively, it is possible for the index-contrasting moieties to be the subunits of a branched or dendritic low molecular weight polymer.

20 [0039] The preferred acrylate monomers are monofunctional. These include 2,4,6-tribromophenylacrylate, pentabromoacrylate, isobornylacrylate, phenylthioethyl acrylate tetrahydrofurfurylacrylate, 1-vinyl-2-pyrrolidinone, asymmetric bis thionaphthyl acrylate, 2-phenoxyethylacrylate, and the like.

25 [0040] In addition to the photoactive monomer, the optical article typically contains a photoinitiator (the photoinitiator and photoactive monomer being part of the overall photoimageable system). The photoinitiator, upon exposure to relatively low levels of the recording light, chemically initiates the polymerization of the monomer, avoiding the need for direct light-induced polymerization of the monomer. The photoinitiator generally should offer a source of species that initiate polymerization of the particular 30 photoactive monomer. Typically, 0.1 to 20 wt. % photoinitiator, based on the weight of the photoimageable system, provides desirable results.

[0041] A variety of photoinitiators known to those skilled in the art and available commercially are suitable for use in the invention. It is advantageous to use a photoinitiator that is sensitive to light in the visible part of the spectrum, particularly at

wavelengths available from conventional laser sources, e.g., the blue and green lines of Ar+ (458, 488, 514 nm) and He-Cd lasers (442 nm), the green line of frequency doubled YAG lasers (532 nm), and the red lines of He-Ne (633 nm) and Kr+ lasers (647 and 676 nm). One advantageous free radical photoinitiator is bis(η -5-2,4-cyclopentadien-1-yl)bis[2,6-difluoro-3-(1H-pyrrol-1-yl)phenyl]titanium, available commercially from Ciba

5 as CGI-784. Another visible free-radical photoinitiator (which requires a co-initiator) is 5,7,diido-3-butoxy-6-fluorone, commercially available from Spectra Group Limited as H-Nu 470. Free-radical photoinitiators of dye-hydrogen donor systems are also possible. Examples of suitable dyes include eosin, rose bengal, erythrosine, and methylene blue,

10 and suitable hydrogen donors include tertiary amines such as n-methyl diethanol amine.

In the case of cationically polymerizable monomers, a cationic photoinitiator is used, such as a sulfonium salt or an iodonium salt. These cationic photoinitiator salts absorb predominantly in the UV portion of the spectrum, and are therefore typically sensitized with a dye to allow use of the visible portion of the spectrum. An example of an

15 alternative visible cationic photoinitiator is (η ₅-2,4-cyclopentadien-1-yl) (η ₆-isopropylbenzene)-iron(II) hexafluorophosphate, available commercial from Ciba as Irgacure 261. It is also conceivable to use other additives in the photoimageable system, e.g., inert diffusing agents having relatively high or low refractive indices.

[0042] Preferably, the photoinitiators are selected according to their sensitivity to the 20 light sources. For example, Irgacure 369, Irgacure 819, and Irgacure 907 are suitable for commercial blue laser systems. CGI-784 is suitable for green laser systems, and CB-650 is suitable for red laser systems. Irgacure and CGI are available from Ciba, CB-650 from Spectra Group.

[0043] Advantageously, for holographic recording, the matrix is a polymer formed by 25 mercaptan-epoxy step polymerization, more advantageously a polymer formed by mercaptan-epoxy step polymerization having a polyether backbone. The polyether backbone offers desirable compatibility with several useful photoactive monomers, particularly vinyl aromatic compounds. Specifically, photoactive monomers selected from styrene, bromostyrene, divinyl benzene, and 4-methylthio-1-vinylnaphthalene 30 (MTVN) have been found to be useful with matrix polymers formed by mercaptan-epoxy step polymerization and having a polyether backbone. A monomer that has more than one index-contrasting moiety and that is also useful with these polyether matrix polymers is 1-(3-(naphth-1-ylthio)propylthio)-4-vinylnaphthalene.

[0044] To be independent, the polymerization reactions for the matrix precursor and the photoactive monomer are selected such that: (a) the reactions proceed by different types of reaction intermediates, (b) neither the intermediate nor the conditions by which the matrix is polymerized will induce substantial polymerization of the photoactive

5 monomer functional groups, and (c) neither the intermediate nor the conditions by which the matrix is polymerized will induce a non-polymerization reaction of the monomer functional groups that causes cross-reaction (between the monomer functional groups and the matrix polymer) or inhibits later polymerization of the monomer functional groups.

According to item (a), if a matrix is polymerized by use of an ionic intermediate, it would 10 be suitable to polymerize the photoactive monomer by use of a free radical reaction. In accordance with item (b), however, the ionic intermediate should not induce substantial polymerization of the photoactive monomer functional groups. Also in accordance with item (b), for example, one must be aware that a photoinitiated free radical matrix polymerization will typically induce a photoinitiated cationic polymerization of a 15 photoactive monomer functional group. Thus, two otherwise independent reactions are not independent for purposes of the invention if both are driven by a single reaction condition. In accordance with item (c), for example, base-catalyzed matrix polymerization should not be performed when the photoactive monomer functional group undergoes a non-polymerization reaction in response to the base, even if polymerization 20 of the monomer functional group is performed by an independent reaction. A specific example is that a base-catalyzed epoxy-mercaptan polymerization should not be used with an acrylate monomer because, although the acrylate is polymerized by a free radical reaction, the acrylate will react with the mercaptans under base catalysis, resulting in a cross-reaction.

25 [0045] Table 1 below illustrates some examples of matrix/photoactive monomer combinations where the matrix polymerization reaction and photoactive monomer polymerization are capable of being independent, and examples where the polymerizations interfere with each other. (Photoactive monomers are horizontal, and matrix polymers are vertical. "X" indicates cross-reaction or monomer polymerization 30 during matrix polymerization. "O" indicates independent reactions. "I" indicates that the photoactive monomer polymerization is inhibited by the reagents or reaction that form the polymeric matrix, e.g., the photoactive monomer functional group is converted to a non-polymerizing group, or chemical species are present after the matrix cure that substantially slow the rate or yield of polymerization of the monomer functional groups.)

Table 1.

	(Meth) acrylates	Styrene Derivatives	Vinyl Ethers	Epoxies
Cationic Epoxy	O	O	X	X
Cationic Vinyl Ethers	O	O	X	X
Epoxy (amine)	X	O	I	X
Epoxy (mercaptan)	X	O	I	X
Unsaturated ester (amine)	X	O	I	X
Unsaturated ester (mercaptan)	X	O	I	X
Hydrosilylation	X	X	X	O
Urethane formation	O	O	O	X

[0046] For purposes of the invention, polymers are considered to be compatible if a blend of the polymers is characterized, in 90° light scattering, by a Rayleigh ratio (R_{90°) less than $7 \times 10^{-3} \text{ cm}^{-1}$. The Rayleigh ratio, R_θ , is a conventionally known property, and is defined as the energy scattered by a unit volume in the direction θ , per steradian, when a medium is illuminated with a unit intensity of unpolarized light, as discussed in M. Kerker, The Scattering of Light and Other Electromagnetic Radiation, Academic Press, San Diego, 1969. The light source used for the measurement is generally a laser having a wavelength in the visible part of the spectrum. Normally, the wavelength intended for use in writing holograms is used. The scattering measurements are made upon a photorecording material that has been flood exposed. The scattered light is collected at an angle of 90° from the incident light, typically by a photodetector. It is possible to place a narrowband filter, centered at the laser wavelength, in front of such a photodetector to block fluorescent light, although such a step is not required. The Rayleigh ratio is typically obtained by comparison to the energy scatter of a reference material having a known Rayleigh ratio.

[0047] Polymer blends which are considered to be miscible, e.g., according to conventional tests such as exhibition of a single glass transition temperature, will

typically be compatible as well, i.e., miscibility is a subset of compatibility. Standard miscibility guidelines and tables are therefrom useful in selecting a compatible blend. However, it is possible for polymer blends that are immiscible to be compatible according to the light scattering test above.

5 [0048] A polymer blend is generally considered to be miscible if the blend exhibits a single glass transition temperature, T_g , as measured by conventional methods. An immiscible blend will typically exhibit two glass transition temperatures corresponding to the T_g values of the individual polymers. T_g testing is most commonly performed by differential scanning calorimetry (DSC), which shows the T_g as a step change in the heat
10 flow (typically the ordinate). The reported T_g is typically the temperature at which the ordinate reaches the mid-point between extrapolated baselines before and after the transition. It is also possible to use Dynamic Mechanical Analysis (DMA) to measure T_g . DMA measures the storage modulus of a material, which drops several orders of magnitude in the glass transition region. It is possible in certain cases for the polymers of
15 a blend to have individual T_g values that are close to each other. In such cases, conventional methods for resolving such overlapping T_g should be used, such as discussed in Brinke et al., "The thermal characterization of multi-component systems by enthalpy relaxation," Thermochimica Acta, 238 (1994), at 75.

20 [0049] Matrix polymer and photopolymer that exhibit miscibility are capable of being selected in several ways. For example, several published compilations of miscible polymers are available, such as O. Olabisi et al, Polymer-Polymer Miscibility, Academic Press, New York, 1979; L.M. Robeson, MMI, Press Symp. Ser., 2, 177, 1982; L.A. Utracki, Polymer Alloys and Blends: Thermodynamics and Rheology, Hanser Publishers, Munich, 1989; and S. Krause in Polymer Handbook, J. Brandrup and E.H.
25 Immergut, Eds., 3rd Ed., Wiley Interscience, New York, 1989, pp. VI 347-370, the disclosures of which are hereby incorporated by reference. Even if a particular polymer of interest is not found in such references, the approach specified allows determination of a compatible photorecording material by employing a control sample.

30 [0050] Determination of miscible or compatible blends is further aided by intermolecular interaction considerations that typically drive miscibility. For example, it is well known that polystyrene and poly(methylvinylether) are miscible because of an attractive interaction between the methyl ether group and the phenyl ring. It is therefore possible to promote miscibility, or at least compatibility, of two polymers by using a methyl ether group in one polymer and a phenyl group in the other polymer. It has also

been demonstrated that immiscible polymers are capable of being made miscible by the incorporation of appropriate functional groups that can provide ionic interactions. (See Z.L. Zhou and A. Eisenberg, J. Polym. Sci., Polym. Phys. Ed., **21** (4), 595, 1983; R. Murali and A. Eisenberg, J. Polym. Sci., Part B: Polym. Phys., **26** (7), 1385, 1988; and 5 A Natansohn et al., Makromol. Chem., Macromol. Symp., **16**, 175, 1988). For example polyisoprene and polystyrene are immiscible. However, when polyisoprene is partially sulfonated (5%), and 4-vinyl pyridine is copolymerized with the polystyrene, the blend of these two functionalized polymers is miscible. It is contemplated that the ionic 10 interaction between the sulfonated groups and the pyridine group (proton transfer) is the driving force that makes this blend miscible. Similarly, polystyrene and poly(ethyl acrylate), which are normally immiscible, have been made miscible by lightly sulfonating the polystyrene. (See R.E. Taylor-Smith and R.A. Register, Macromolecules, **26**, 2802, 1993.) Charge-transfer has also been used to make miscible polymers that are otherwise 15 immiscible. For example it has been demonstrated that, although poly(methyl acrylate) and poly(methyl methacrylate) are immiscible, blends in which the former is copolymerized with (N-ethylcarbazol-3-yl)methyl acrylate (electron donor) and the latter is copolymerized with 2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate (electron acceptor) are miscible, provided the right amounts of donor and acceptor are used. (See M.C. Piton and A. Natansohn, Macromolecules, **28**, 15, 1995.) Poly(methyl methacrylate) and 20 polystyrene are also capable of being made miscible using the corresponding donor-acceptor co-monomers (See M.C. Piton and A. Natansohn, Macromolecules, **28**, 1605, 1995).

[0051] A variety of test methods exist for evaluating the miscibility or compatibility of polymers, as reflected in the recent overview published in A. Hale and H. Bair, Ch. 25 4 - "Polymer Blends and Block Copolymers," Thermal Characterization of Polymeric Materials, 2nd Ed., Academic Press, 1997. For example, in the realm of optical methods, opacity typically indicates a two-phase material, whereas clarity generally indicates a compatible system. Other methods for evaluating miscibility include neutron scattering, infrared spectroscopy (IR), nuclear magnetic resonance (NMR), x-ray scattering and 30 diffraction, fluorescence, Brillouin scattering, melt titration, calorimetry, and chemiluminescence. See, for example, L. Robeson, supra; S. Krause, Chemtracts - Macromol. Chem., **2**, 367, 1991a; D. Vessely in Polymer Blends and Alloys, M.J. Folkes and P.S. Hope, Eds., Blackie Academic and Professional, Glasgow, pp. 103-125; M.M. Coleman et al. Specific Interactions and the Miscibility of Polymer Blends,

Technomic Publishing, Lancaster, PA, 1991; A. Garton, Infrared Spectroscopy of Polymer Blends, Composites and Surfaces, Hanser, New York, 1992; L.W. Kelts et al., Macromolecules, 26, 2941, 1993; and J.L. White and P.A. Mirau, Macromolecules, 26, 3049, 1993; J.L. White and P.A. Mirau, Macromolecules, 27, 1648, 1994; and C.A.

5 Cruz et al., Macromolecules, 12, 726, 1979; and C.J. Landry et al., Macromolecules, 26, 35, 1993.

[0052] Compatibility has also been promoted in otherwise incompatible polymers by incorporating reactive groups into the polymer matrix, where such groups are capable of reacting with the photoactive monomer during the holographic recording step. Some of 10 the photoactive monomer will thereby be grafted onto the matrix during recording. If there are enough of these grafts, it is possible to prevent or reduce phase separation during recording. However, if the refractive index of the grafted moiety and of the monomer are relatively similar, too many grafts, e.g., more than 30% of monomers grafted to the matrix, will tend to undesirably reduce refractive index contrast.

15 [0053] A holographic recording medium of the invention is formed by adequately supporting the photorecording material, such that holographic writing and reading is possible. Typically, fabrication of the medium involves depositing the matrix precursor/photoimageable system mixture between two plates using, for example, a gasket to contain the mixture. The plates are typically glass, but it is also possible to use 20 other materials transparent to the radiation used to write data, e.g., a plastic such as polycarbonate or poly(methyl methacrylate). It is possible to use spacers between the plates to maintain a desired thickness for the recording medium. During the matrix cure, it is possible for shrinkage in the material to create stress in the plates, such stress altering the parallelism and/or spacing of the plates and thereby detrimentally affecting the 25 medium's optical properties. To reduce such effects, it is useful to place the plates in an apparatus containing mounts, e.g., vacuum chucks, capable of being adjusted in response to changes in parallelism and/or spacing. In such an apparatus, it is possible to monitor the parallelism in real-time by use of a conventional interferometric method, and make any necessary adjustments during the cure. Such a method is discussed, for example, in 30 U.S. patent application Serial No. 08/867,563, the disclosure of which is hereby incorporated by reference. The photorecording material of the invention is also capable of being supported in other ways. For instance, it is conceivable to dispose the matrix precursor/photoimageable system mixture into the pores of a substrate, e.g., a nanoporous glass material such as Vycor, prior to matrix cure. More conventional polymer

processing is also envisioned, e.g., closed mold formation or sheet extrusion. A stratified medium is also contemplated, i.e., a medium containing multiple substrates, e.g., glass, with layers of photorecording material disposed between the substrates.

[0054] The medium of the invention is then capable of being used in a holographic system such as discussed previously. The amount of information capable of being stored in a holographic medium is proportional to the product of: the refractive index contrast, Δn , of the photorecording material, and the thickness, d , of the photorecording material.

(The refractive index contrast, Δn , is conventionally known, and is defined as the amplitude of the sinusoidal variations in the refractive index of a material in which a

10 plane-wave, volume hologram has been written. The refractive index varies as:

$n(x) = n_0 + \Delta n \cos(K_x)$, where $n(x)$ is the spatially varying refractive index, x is the position vector, K is the grating wavevector, and n_0 is the baseline refractive index of the medium. See, e.g., P. Hariharan, Optical Holography: Principles, Techniques, and Applications, Cambridge University Press, Cambridge, 1991, at 44.) The Δn of a material

15 typically calculated from the diffraction efficiency or efficiencies of a single volume hologram or a multiplexed set of volume holograms recorded in a medium. The Δn is associated with a medium before writing, but is observed by measurement performed after recording. Advantageously, the photorecording material of the invention exhibits a Δ of 3×10^{-3} or higher.

20 [0055] Examples of other optical articles include beam filters, beam steerers or deflectors, and optical couplers. (See, e.g., L. Solymar and D. Cooke, Volume Holography and Volume Gratings, Academic Press, 315-327 (1981), the disclosure of which is hereby incorporated by reference.) A beam filter separates part of an incident laser beam that is traveling along a particular angle from the rest of the beam.

25 Specifically, the Bragg selectivity of a thick transmission hologram is able to selectively diffract light along a particular angle of incidence, while light along other angle travels undeflected through the hologram. (See, e.g., J.E. Ludman et al., "Very thick holographic nonspatial filtering of laser beams," Optical Engineering, Vol. 36, No. 6, 1700 (1997), the disclosure of which is hereby incorporated by reference.) A beam

30 steerer is a hologram that deflects light incident at the Bragg angle. An optical coupler is typically a combination of beam deflectors that steer light from a source to a target. These articles, typically referred to as holographic optical elements, are fabricated by imaging a particular optical interference pattern within a recording medium, as discussed

previously with respect to data storage. Medium for these holographic optical elements are capable of being formed by the techniques discussed herein for recording media or waveguides.

[0056] As mentioned previously, the material principles discussed herein are applicable not only to hologram formation, but also to formation of optical transmission devices such as waveguides. Polymeric optical waveguides are discussed for example in B.L. Booth, "Optical Interconnection Polymers," in Polymers for Lightwave and

Integrated Optics, Technology and Applications, L.A. Hornak, ed., Marcel Dekker, Inc.

(1992); U.S. Patent No. 5,292,620; and U.S. Patent No. 5,219,710, the disclosures of

which are hereby incorporated by reference. Essentially, the recording material of the invention is irradiated in a desired waveguide pattern to provide refractive index contrast between the waveguide pattern and the surrounding (cladding) material. It is possible for exposure to be performed, for example, by a focused laser light or by use of a mask with a non-focused light source. Generally, a single layer is exposed in this manner to provide

the waveguide pattern, and additional layers are added to complete the cladding, thereby completing the waveguide. The process is discussed for example at pages 235-36 of Booth, supra, and Cols. 5 and 6 of U.S. Patent No. 5,292,620. A benefit of the invention is that by using conventional molding techniques, it is possible to mold the matrix/photoimageable system mixture into a variety of shapes prior to matrix cure. For

example, the matrix/photoimageable system mixture is able to be molded into ridge waveguides, wherein refractive index patterns are then written into the molded structures. It is thereby possible to easily form structures such as Bragg gratings. This feature of the invention increases the breadth of applications in which such polymeric waveguides would be useful.

[0057] The invention will be further clarified by the following examples, which are intended to be exemplary.

Examples and Comparative Examples

[0058] To fabricate the high performance recording article, the NCO-terminated prepolymer and polyol must first be reacted to form a matrix in which the acrylate

monomer, which remains unreacted, will reside.

[0059] As the reaction of the NCO-terminated prepolymer and polyol are two-component system, the NCO-terminated prepolymer, acrylate monomer, photoinitiator, and thermal stabilizers are predissolved to form a homogeneous solution before charging into one of the holding tanks of a Posiratio two-component metering, mixing and

dispensing machine, available from Liquid Control Corp. The polyol, tin catalyst, and other additives are premixed and charged into another holding tank. Each tank is then degassed, adjusting dispensing of materials from the tanks to the desired amount according to the procedures outlined by Liquid Control.

5 [0060] Precise and accurate mixing of the two components, free of entrapped air bubbles, is carried out by metering the liquid from both tanks simultaneously into a helical element static mixer.

[0061] To form a holographic recording article, the desired amount of the well-mixed solution is dispensed onto the inner surface of the bottom substrate held by one of the 10 parallel plate. The upper substrate, which is held by the other parallel plate, is then brought down to come in contact with the solution and held at a predetermined distance from the bottom plate, according to the procedures described in US Patent 5,932,045 issued August 3, 1999, the disclosure of which is hereby incorporated by reference. The entire set-up is held till the solution becomes solidified to assure an optically flat article is 15 produced.

[0062] High performance holographic recording articles are characterized by low shrinkage, dynamic range, and sensitivity. Low shrinkage will assure non-degradation of the recorded holograms and total fidelity of the holographic data to be recovered. Low shrinkage in the range of less than 0.2 % is required. The dynamic range of a holographic 20 recording medium is typically characterized by the parameter, M/#, a measure of how many holograms of a give average diffraction efficiency can be stored in a common volume. The M/# is determined by both the refractive index contrast and thickness of a medium. Typical values of M/# are 1.5 or better. The photosensitivity is characterized by the total exposure time required to consume the dynamic range of the media. The 25 sensitivity can be in the range of 25 to 120 seconds.

[0063] Details of the measurements of the recording-induced shrinkage, M/# / 200 μm , and sensitivity are described in detail in Applied Physics Letters, Volume 73, Number 10, p. 1337-1339, 7 September 1998, which is incorporated herein by reference. Angle-multiplexing a series of plane-wave holograms into the recording medium produce 30 these measurements. A frequency-doubled diode-pumped Nd:YAG laser used for recording and recovery of the multiplexed holograms was spatially filtered and collimated by a lens to yield a plane-wave source of light. The light was then split into two beams by polarizing beam splitters and half-wave plates and intersected at the sample at an external angle of 44°. The power of each beam was 2 mW and the spot diameter was 4

mm. Each hologram is written with a predetermined exposure time. After recording, the material was allowed to sit in the dark for 20 minutes and then flood cured with a Xenon lamp filtered to transmit wavelengths longer than 530 nm.

Comparative Example 1

5 [0064] A solution was prepared containing 89.25 wt.% phenoxyethyl acrylate (photoactive monomer), 10.11 wt.% ethoxylated bisphenol-A diacrylate (photoactive monomer), 0.5 wt.% Ciba CGI-784 (identified previously) (photoinitiator), and 0.14 wt.% dibutyltin dilaurate (catalyst for matrix formation). 0.0904 g of the solution was added to a vial containing 0.2784 g diisocyanate-terminated polypropylene glycol (MW=2471) 10 (matrix precursor) and 0.05 g α,ω -dihydroxypolypropylene glycol (MW=425) (matrix precursor). The mixture was thoroughly mixed and allowed to polymerize overnight at room temperature, while protected from light. The polymerization was a step 15 polymerization of the isocyanate groups with the hydroxyl groups to form a polyurethane with dissolved acrylate monomers. The mixture appeared clear and transparent to the naked eye. Upon exposure to an intense tungsten light, which initiated polymerization of the acrylate monomers, the material turned milky white, indicating that the polyurethane matrix and acrylate polymers were not compatible.

15 [0065] Consultation of the polymer miscibility table published by Krause, referenced above, shows that polyurethanes are miscible, and thus compatible, with Saran®, a 20 chlorinated polymer.

Comparative Example 2

[0066] The following comparative example was carried out using a Posiratio two-component metering, mixing and dispensing machine, available from Liquid Control Corp. Products in each component were pre -dissolved and mixed into a homogeneous 25 solution, and the two solutions were then transferred into the corresponding A and B holding tanks of the machine. Each tank was then degassed. Dispensing of materials from the tanks was adjusted to the desired amount according to the procedures outlined by Liquid Control.

[0067] Precise and accurate mixing of the two components, free of entrapped air 30 bubbles, was carried out by metering the liquid from both tanks simultaneously into a helical element static mixer. The resultant mixture, the combined weight metered out of each component, was dispensed onto a small tin dish and observed for:

- (a) Exotherm start
- (b) Exotherm peak
- (c) Soft gel
- (d) Fabrication completed
- (e) Shrinkage
- (f) Dynamic range, M/#/200 μ m
- (g) Sensitivity, seconds to write 80 % of the sample

[0068] The above mentioned properties were measured as follows:

[0069] The exotherm start, i.e., when the rise in the temperature of the material dispensed on the dish begins, which indicates the start of the reaction, was measured by a

5 thermocouple or thermometer inserted within the material dispensed on the dish. The

[0070] The exotherm peak was recorded by monitoring the time when the temperature of the thermocouple or thermometer peaks.

[0071] The soft-gel state was monitored by finger pressing the material dispensed on the dish. Soft-gel state was the state when the surface of the material dispensed on the

10 dish was not sticky and the material would not flow when the dish was tilted vertically, but the gel could still be deformed by finger pressing.

[0072] Solidification was also determined by finger pressing the material dispensed on the dish. Solidification occurred when finger pressing could not deform the material dispensed on the dish.

15 [0073] The shrinkage (occurring primarily in the thickness of the medium) is determined by measuring the Bragg detuning (the shift in the readout angle) of the angle multiplexed holograms. The quantitative relationship between the physical shrinkage of the material and the Bragg detuning is described in detail in the above reference, i.e., Applied Physics Letters, Volume 73, Number 10, p. 1337-1339, 7 September 1998.

20 [0074] The M/# is defined to be the dynamic range of the recording material. The M/# is measured by multiplexing a series of holograms with exposure times set to consume all of the photoactive material in the media. The M/# is defined to be the sum of the square roots of the diffraction efficiencies of all of the multiplexed holograms. Because the M/# depends on the thickness of the media, the quantities listed in the

25 examples are scaled to 200 μ m thicknesses.

[0075] The sensitivity is measured by the cumulative exposure time required to reach 80% of the total M/# of the recording medium. The higher the sensitivity of the material, the shorter the cumulative exposure time required to reach 80% of the total M/#.

5 [0076] The formulation of the composition for Comparative Example 2 and the properties of the material dispensed on the dish are shown in Table 2. Precise and accurate mixing of the two components, free of entrapped air bubbles, was carried out by metering the liquid from both tanks simultaneously into a helical element static mixer. The resultant mixture, the combined weight metered out of each component, was dispensed in between two parallel 3"x 3" pieces of clear glass plates. The following 10 times were observed for comparison:

[0077] The time it took for the exotherm to start that was defined as the time it took for the temperature to rise from 24°C to 30°C.

[0078] The time it took for the exotherm to peak.

15 [0079] The time at soft gel. At the soft-gel state, the two pieces of glass plates could still be slid away from each other.

[0080] The time for the completion of fabrication when the mixture was solid and the two pieces of glass could not be slid away from each other.

Table 2.

Component 1, Tank A	Baytech WE-180	415.7 gm
	Tribromophenylacrylate	38.0 gm
	CGI-784	8.44 gm
	BHT	210 mg
Component 2, Tank B	Polypropylene Oxide Triol	577 gm
	t-Butylperoxide	310 μ l
	Dibutyltindilaurate	10.4 gm
<i>Fabricate the articles</i>		
Amount metered out of component 1, Tank A	10.0 gm	
Amount metered out of component 2, Tank B	13.0 gm	
Exotherm start, (temperature rises from 24°C to 30°C)	5 min	
Time for exotherm to peak	15 min.	
Exotherm peak temperature	39.8°C	
Soft gel	35 min.	
Fabrication completed	3 hours	
Shrinkage	0.1 %	
Dynamic range, M/#/200 μ m	2.4	
Sensitivity, seconds to write 80 % of the sample	25	

1) Baytech WE-180, available from Bayer, is a 50/50 blend of biscyclohexylmethane diisocyanate and a NCO-terminated prepolymer based on biscyclohexylmethane diisocyanate and polytetramethylene glycol.

5

2) Polypropylene Oxide Triol of 1000 molecular weight.

Example 1

10 [0081] Samples of Example 1 were prepared and evaluated in accordance with the procedures of Comparative Example 2 except using the following components resulting in the properties shown in Table 3 below.

Table 3.

Component 1, Tank A	Baytech WE-180	200 gm
	Mondur ML	200 gm
	Tribromophenylacrylate	44.93 gm
	CGI-784	9.84 gm
	BHT	254 mg
Component 2, Tank B	Polypropylene Oxide Triol	807 gm
	t-Butylperoxide	310 μ l
	Dibutyltindilaurate	12.5 gm
<i>Fabricate the articles</i>		
Amount metered out of component 1, Tank A	10.0 gm	
Amount metered out of component 2, Tank B	18.0 gm	
Exotherm start, (temperature rises from 24°C to 30°C)	1 min	
Time for exotherm to peak	2 min	
Exotherm peak temperature	71°C	
Soft gel	3 min.	
Fabrication completed	17 min	
Shrinkage	0.12 %	
Dynamic range, M/#/200 μ m	1.8	
Sensitivity, seconds to write 80 % of the sample	67	

Mondur ML is liquid diphenylmethane diisocyanate available from Bayer.

5

Example 2

[0082] Samples of Example 2 were prepared and evaluated in accordance with the procedures of Comparative Example 2 except using the following components resulting in the properties shown in Table 4 below.

Table 4.

Component 1, Tank A	Baytech WE-180	200 gm
	Mondur ML	200 gm
	Mondur TD	44.4 gm
	Pentabromooacrylate	76.48 gm
	CGI-784	11.93 gm
	BHT	223 mg
Component 2, Tank B	Polypropylene Oxide Triol	996.5 gm
	t-Butylperoxide	474 μ l
	Dibutyltindilaurate	11.2 gm
<i>Fabricate the articles</i>		
Amount metered out of component 1, Tank A	10.0 gm	
Amount metered out of component 2, Tank B	18.4 gm	
Exotherm start, (temperature rises from 24°C to 30°C)	1 min	
Time for exotherm to peak	2 min	
Exotherm peak temperature	63°C	
Soft gel	3 min.	
Fabrication completed	15 min	
Shrinkage	0.1 %	
Dynamic range, M/#/200 μ m	2.1	
Sensitivity, seconds to write 80 % of the sample	85	

Mondur TD is toluene diisocyanate (TDI) available from Bayer.

5

Example 3

[0083] Samples of Example 3 were prepared and evaluated in accordance with the procedures of Comparative Example 2 except using the following components resulting in the properties shown in Table 5 below.

10

Table 5.

Component 1, Tank A	Baytech MP-160	400.0 gm
	Mondur TD	60.0 gm
	Tribromophenylacrylate	64.22 gm
	CGI-784	10.0 gm
	BHT	210 mg
Component 2, Tank B	Polypropylene Oxide Triol	750.0 gm
	t-Butylperoxide	398 μ l
	Dibutyltindilaurate	10.2 gm
<i>Fabricate the articles</i>		
Amount metered out of component 1, Tank A		10.0 gm
Amount metered out of component 2, Tank B		18.7 gm
Exotherm start, (temperature rises from 24°C to 30°C)		0.5 min
Time for exotherm to peak		1 min
Exotherm peak temperature		56°C
Soft gel		2 min.
Fabrication completed		15 min
Shrinkage		0.1 %
Dynamic range, M/#/200 μ m		1.8
Sensitivity, seconds to write 80 % of the sample		94

Baytech MP-160, available from Bayer, is a NCO-terminated prepolymer based on diphenylmethane diisocyanate and polypropylene ether glycol.

5

Example 4

[0084] Samples of Example 2 were prepared and evaluated in accordance with the procedures of Comparative Example 2 except using the following components resulting in the properties shown in Table 6 below.

Table 6.

Component 1, Tank A	Baytech WE-180	180 gm
	Desmodur N3200	120 gm
	Tribromoacrylate	33.9 gm
	BHT	188 mg
Component 2, Tank B	Polypropylene Oxide Triol	300 gm
	PMEG 1000	306 gm
	CGI 784	7.425 gm
	t-Butylperoxide	2.9 ml
	Dibutyltindilaurate	9.47 gm
<i>Fabricate the articles</i>		
Amount metered out of component 1, Tank A		1.13 gm
Amount metered out of component 2, Tank B		2.0 gm
Exotherm start, (temperature rises from 24°C to 30°C)		1 min
Time for exotherm to peak		5 min
Exotherm peak temperature		47°C
Soft gel		8 min.
Fabrication completed		17 min
Shrinkage		0.09%
Dynamic range, M/#/200 µm		2.15
Sensitivity, seconds to write 80 % of the sample		26

Desmodur N3200 is the biuret derivative of HDI, available from Bayer.

5 PMEG 1000 is polytetramethylene ether diol having 1000 molecular weight.

Polypropylene Oxide Triol of 1500 molecular weight.

[0085] The above description is presented to enable a person skilled in the art to make and use the invention, and is provided in the context of a particular application and its requirements. Various modifications to the preferred embodiments will be readily apparent to those skilled in the art, and the generic principles defined herein may be applied to other embodiments and applications without departing from the spirit and

scope of the invention. Thus, this invention is not intended to be limited to the embodiments shown, but is to be accorded the widest scope consistent with the principles and features disclosed herein.

[0086] This application discloses several numerical range limitations. Persons skilled in the art would recognize that the numerical ranges disclosed inherently support any range within the disclosed numerical ranges even though a precise range limitation is not stated verbatim in the specification because this invention can be practiced throughout the disclosed numerical ranges. A holding to the contrary would "let form triumph over substance" and allow the written description requirement to eviscerate claims that might 5 be narrowed during prosecution simply because the applicants broadly disclose in this application but then might narrow their claims during prosecution. Finally, the entire disclosure of the patents and publications referred in this application are hereby 10 incorporated herein by reference.

Claims:

1. An optical article comprising a photoactive material and a polymer matrix formed by a polymerizing reaction of a material comprising component 1 and component 2, said component 1 comprises a NCO-terminated pre-polymer and said component 2

5 comprises a polyol;

wherein said material has an exotherm peak occurring within 12 minutes after mixing said component 1 and said component 2.

10 2. The optical article of claim 1, wherein the polymerization reaction is selected from a group consisting of a urethane formation reaction, an urea formation reaction and combinations thereof.

15 3. The optical article of claim 1, wherein said component 1 comprises a substance selected from the group consisting of aromatic isocyanate, aliphatic isocyanate and combinations thereof.

4. The optical article of claim 1, wherein said component 1 comprises a substance selected from the group consisting of aromatic diisocyanate, hexamethylene diisocyanate, a derivative of hexamethylene diisocyanate and combinations thereof.

20 5. The optical article of claim 1, wherein said polyol comprises a polyol of polypropylene oxide.

25 6. The optical article of claim 5, wherein said component 2 further comprises a polytetramethylene ether diol.

7. The optical article of claim 1, wherein the photoactive material is a photoactive monomer.

30 8. The optical article of claim 7, wherein the photoactive monomer is an acrylate monomer.

9. The optical article of claim 1, wherein the optical article is a holographic recording medium having a thickness greater than 200 μm and Δn of 3×10^{-3} or higher.

5 10. The optical article of claim 1, wherein the optical article is an optical waveguide.

11. The optical article of claim 1, wherein the optical article has a writing induced shrinkage of less than 0.25 percent.

10 12. The optical article of claim 1, wherein the optical article is a holographic recording medium.

15 13. The optical article of claim 1, wherein said material has an exotherm peak occurring within 5 minutes after mixing said component 1 and said component 2 and said material has a soft gel within 15 minutes after mixing said component 1 and said component 2.

20 14. The optical article of claim 1, wherein said material has an exotherm peak occurring within 3 minutes after mixing said component 1 and said component 2 and said material has a soft gel within 5 minutes after mixing said component 1 and said component 2.

25 15. An optical article comprising a photoactive material and a polymer matrix formed by a polymerizing reaction of a material comprising component 1 and component 2, said component 1 comprises biscyclohexylmethane diisocyanate, a NCO-terminated prepolymer formed by a reaction of biscyclohexylmethane diisocyanate and polytetramethylene glycol, butyrate hydroxytoluene and a derivative of hexamethylene diisocyanate, and said component 2 comprises a polyol of polypropylene oxide and a polyol of polytetramethylene ether;

30 wherein said material has an exotherm peak occurring within 12 minutes after mixing said component 1 and said component 2.

16. An optical article comprising a photoactive material and a polymer matrix formed by a polymerizing reaction of a material comprising component 1 and component 2, said component 1 comprises a NCO-terminated pre-polymer selected from the group consisting of diphenylmethane diisocyanate, toluene diisocyanate, hexamethylene diisocyanate and a derivative of hexamethylene diisocyanate, and said component 2 comprises a polyol of polypropylene oxide;

wherein said material has an exotherm peak occurring within 12 minutes after mixing said component 1 and said component 2.

10 17. A method of manufacturing an optical article, comprising:
mixing component 1 and component 2 to form a material comprising a
photoactive material and
reacting ingredients of said material,
wherein said component 1 comprises a NCO-terminated pre-polymer and said
15 component 2 comprises a polyol, and said material has an exotherm peak occurring
within 12 minutes after mixing said component 1 and said component 2.

18. The method of claim 17, wherein said reacting comprises a polymerization reaction selected from a group consisting of a urethane formation reaction, an urea formation reaction, cationic epoxy polymerization, cationic vinyl ether polymerization, cationic alkenyl ether polymerization, cationic allyl ether polymerization, cationic ketene acetal polymerization, epoxy-amine step polymerization, epoxy-mercaptan step polymerization, unsaturated ester-amine step polymerization, unsaturated ester-mercaptan step polymerization, a hydrosilylation reaction and combinations thereof.

25 19. The method of claim 17, wherein said component 1 comprises a substance selected from the group consisting of aromatic isocyanate, aliphatic isocyanate and combinations thereof.

30 20. The method of claim 17, wherein said component 1 comprises a substance selected from the group consisting of aromatic diisocyanate, hexamethylene diisocyanate, a derivative of hexamethylene diisocyanate and combinations thereof.

21. The method of claim 17, wherein said polyol comprises a polyol of polypropylene oxide.

5 22. The method of claim 21, wherein said component 2 further comprises a polytetramethylene ether diol.

23. The method of claim 17, wherein the photoactive material is a photoactive monomer.

10 24. The method of claim 23, wherein the photoactive monomer is an acrylate monomer.

15 25. The method of claim 17, wherein said material has an exotherm peak occurring within 5 minutes after mixing said component 1 and said component 2 and said material has a soft gel within 15 minutes after mixing said component 1 and said component 2.

20 26. The method of claim 17, wherein said material has an exotherm peak occurring within 3 minutes after mixing said component 1 and said component 2 and said material has a soft gel within 5 minutes after mixing said component 1 and said component 2.

25 27. A method of manufacturing an optical article, comprising:
mixing a photoactive material and a material comprising component 1 and component 2, said component 1 comprises biscyclohexylmethane diisocyanate, a NCO-terminated prepolymer formed by a reaction of biscyclohexylmethane diisocyanate and polytetramethylene glycol, butyrate hydroxytoluene and a derivative of hexamethylene diisocyanate, and said component 2 comprises a polyol of polypropylene oxide and a polyol of polytetramethylene ether, and
30 reacting ingredients of said material;
wherein said material has an exotherm peak occurring within 12 minutes after mixing said component 1 and said component 2 and said material has a soft gel within 30 minutes after mixing said component 1 and said component 2.

28. A method of manufacturing an optical article, comprising:
mixing a photoactive material and a material comprising component 1 and
component 2, said component 1 comprises a NCO-terminated pre-polymer selected from
the group consisting of diphenylmethane diisocyanate, toluene diisocyanate,
5 hexamethylene diisocyanate and a derivative of hexamethylene diisocyanate, and said
component 2 comprises a polyol of polypropylene oxide, and
reacting ingredients of said material;
wherein said material has an exotherm peak occurring within 12 minutes after
mixing said component 1 and said component 2 and said material has a soft gel within 30
10 minutes after mixing said component 1 and said component 2.

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/US 02/24926A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G18/10 G11B7/26 G03H1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G G11B G03H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 959 775 A (JOSEPH ET AL) 28 September 1999 (1999-09-28) column 4, line 15 -column 8, line 35; claims 1,3-11 ----	1-4
A	DATABASE WPI Week 9402 Derwent Publications Ltd., London, GB; AN 1994-016313 XP002220015 "hologram record medium" & JP 05 323850 A (DAINIPPON PRINTING), 7 December 1993 (1993-12-07) abstract ---- -/-	1

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
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Date of the actual completion of the International search	Date of mailing of the International search report
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Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Bourgonje, A

INTERNATIONAL SEARCH REPORT

Inte ~~rnal~~ Application No
PCT/US 02/24926

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Week 9017 Derwent Publications Ltd., London, GB; AN 1990-128677 XP002220016 "Photo record medium" & JP 02 078033 A (CANON), 19 March 1990 (1990-03-19) abstract</p> <p>-----</p>	1

INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No
PCT/US 02/24926

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 5959775	A 28-09-1999	AU 7103698	A 12-07-1999	
		CA 2315059	A1 01-07-1999	
		CN 1283275	T 07-02-2001	
		EP 1042693	A1 11-10-2000	
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JP 5323850	A 07-12-1993	NONE		
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